Possible weathering of the brick matrix when exposed to water

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Possible weathering of the brick matrix when exposed to water with different pH

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ABSTRACT:

The main reasons for deterioration of bricks are frost, crystallization pressure and chemical exposure. Despite of this the effect of chemical exposure is limited clarified.

Depending on the brick type the original pH of bricks are 9-10. Though bricks can to subjected to water in shape of acid rain with a pH as low as 3. The exposure of acid rain and rain water to bricks is expected to have an influence on the brick matrix dependent on the specific exposure but to which extend? The present work is a systematic test of the influence of the pH on the brick matrix where the effect of water with different well-defined pH values are examined to investigate the long term effect of acid rain or other reasons causing pH changes to bricks (as e.g. electrokinetic treatment).

Through capillary suction, macro pictures from the exposed surfaces, measurement of the pH and electrical conductivity it seemed that there is a consistence with the literature of the glassy phase describing ion exchange at low pH and break down of the lattice in the glassy structure at high pH.

At present remains examination of polished sections with SEM/EDX, measurements of each of the ionic contents in the brick matrix and new series with a longer exposure time to make more sound conclusions. This work is ongoing.

Keywords: Brick matrix, pH, weathering

1 INTRODUCTION

Bricks exposed to acidic water as a consequence of sulphuric acid from the atmosphere results in decreasing strength compared to bricks only subjected to distilled water. In [1] the firing degrees influence on deterioration caused by acid exposure was investigated on brick specimens fired at 900˚C, 1040 ˚C and 1150 ˚C. The brick specimens were submerged into 10 % (H_2SO_4, HNO_3) solutions with a pH of zero until relative little weight loss was found after 250 days with the aim to find eventual difference in acid resistance in bricks related to firing degrees and the type of acid. Significant higher acid resistance was found for bricks fired at 1150 ˚C than at 900 ˚C and H_2SO_4 resulted in a higher cation reduction than HNO_3. In [2] the natural weathering effect on bricks placed at the ground and in construction was measured. A reduced pH (8.2-8.8) was measured in bricks placed at the ground highly exposed to rain though possessing an average ion content, whereas bricks in construction behind plaster had pH similar to new bricks (9.3) but with an untraditionally high ion content. In the study it was also found that non-exposed fired bricks manufactured of a clay mixture with a

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relative high carbonate content (yellow brick) were found to have some resistance against acidification compared to non-exposed bricks manufactured of a clay mixture with a relative low carbonate content (red brick).

In [3] the long-term effect of water run-off at a brick was studied on a brick from the 16th century in Venice, showing significant erosion of the surface, however uneven in erosion due to differences in vitrification. They also studied a local Venetian brick from the 12th century where the glassy phase was eroded and the platy minerals were still present representing extreme environmental expose.

The aim with the present work is systematically to clarify the weathering effect caused by pH changes, ranging from pH 3 induced by acid rain to pH 11 as a consequence of contact with alkaline materials (e.g. lime mortar, cement). The possible influence of such actions is to be clarified. This was done by regarding the theory for the glassy phase in relation to acidic and alkaline exposure as [3] showed that changes in bricks occur in this element being dependent on chemical stability in the brick and the environment. This was compared with results for brick specimens submerged into solutions with varying pH and duration regarding measured matrix pH and electrical conductivity, macroscopic material properties and macroscopic pictures.

2 GLASS PHASE THEORY

The definition of glass from the American Society for Testing Materials and subsequently used in the German norm 868 is: Glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallizing [4]. Traditional mechanical produced glass consists of 73% SiO_2, 1% Al_2O_3, 11 % CaO (+MgO), 14 % Na_2O and 1% K_2O [4].

SiO_4 tetraeder chain is the determining component in Crystalline and silicates and the numbers of crosslinks of the oxides between the chain is determining for the overall stability together with the variation of the Si-O composition (e.g. Si-O-Si or Si-O-Al) [4]. According to [5] are Si-O-Si bonds very stable at pH between 2 and 7. Whereas Al-O bonds at pH below 4 easy through acid catalyzed hydrolyse deteriorates. Hereby can the lattice be opened and exchange of cations in the lattice against H^+ can come into existence. In an alkaline environment SiO_2 can split the network due to the effect of the OH^- [4]. According to [6] is the critical alkali pH 8.5. In [6] it was also pointed out that water independent dissociate into H^+ and OH^-. The effect of the dissociation is dependent on the surface area to volume ratio where increasing ratios results in an increased effect. [6] showed experimentally how increasing temperatures resulted in an increased effect. Hydrogen takes part in the ion exchange reaction or is accumulated at the negatively charged glass surface. As a consequence the OH^- concentration increases and the pH value increases resulting in increased leaching of the glass matrix. According to [4] is ion exchange between acidic water solutions and glass possible due to mobility inside the glass resulting in reduced alkalinity. The amount of dissolving cations entering the solution is increasing and proportional to the square root of the time and simultaneously followed by H_2O molecules entering the glass where this amount is dependent of the specific glass type (ion-exchange process). In an alkaline environment the OH^- will react with SiO_2 and can result in a break-up of the lattice to soluble silicic acid which will be equal to a complete dissolution of the glass. The dissolution of the glass increases with increasing pH were the dissolved amount of glass is linear with time (dissolution of the lattice). It is presumed that water reaction is similar to the reactions in acidic solutions on glass meaning by an ion-exchange process. Both the velocity of ion-exhange caused by acid solutions, water solutions (with their natural pH) and the dissolution of the lattice in case of alkaline solutions are dependent of the composition of the glass [4].

Leaching in bricks made of harbor sediments and commercial bricks were investigated in the pH range 4-11 [7]. They showed that leachbility is high at pH 4 and decreases with increasing pH-values

(Mg, Ca, V, Cr, Mn, Ni, Cu, Zn, As, Sr, Cd, Ba) exceptions are SO_4, K and Mo, these parameters show constant leachability over the whole pH-range examined. Al and Si showed minimum leachability in the neutral to slightly alkaline pH-range, with increasing leachability at both increasing and decreasing pH-values. Besides the influence from the pH leachabiility is also dependent on the grain size where reduced grans size results in increasing leachability as a consequence of increasing specific surface areas. According to [3] at pH above 9 dissolution of silica glasses occur whereas pH down to 2 will not result in increased dissolution than removed by water alone as the acid neutralizes the leached alkalis.

3 METHODS

The macroscopic effect was examined through capillary suction. For this determination the brick specimens were submerged into distilled water for 6 hours which was considered to be have an insignificant influence on the result compared to the prior submersion of the brick specimens into solutions with pH varying between 3 and 11 for 24 to 144 days. Following the brick specimens were vacuum saturated with distilled water and weighted above and below water to determine the open porosity and the density

The pH was measured with electrode MeterLab®CDM220 and the electrical conductivity with electrode MeterLab®CDM210 after settling of the agitated sample (for 5 minutes or until a clear liquid came into existence).
The pictures were taken with a Nikon D610 camera. The camera was placed in a mounting at a distance of 6 cm from the photographed surface. The specimens were illuminated with Kaiser RB 5000 Daylight Copy Light Set.

4 EXPERIMENTAL

Bricks where submerged in liquids with pH 3, 5, 7, 9 and 11 (pH adjustment was carried out with H_2SO_4 and NaOH) with three different submersion durations at each pH value, see table 1.

Table 1. Experimental overview

	pH of the solutions	**Time of exposure [Days]**
Series 1	3, 5, 7, 9, 11	24
Series 2	3, 5, 7, 9, 11	120
Series 3	3, 5, 7, 9, 11	144

The brick specimens were after ended submersion in the solutions and capillary suction divided into two equal pieces. One piece (a) was subsequently to be used for preparation of polished sections and the other half (b) was used for determination of chemical conditions in the brick matrix. A cut was made in the brick halves (b) 0.9-1 cm parallel to the smallest exposed surface. The chosen distance of the cut to the exposed surface was the smallest possible distance to the exposed surface in relation to the cutting machine and the expected depth in which the matrix was influenced on basis of the experiences in [1]. In [1] the degree of leaching from bricks in an acidic solution was assessed on basis of mass changes and after 250 days no significant mass changes were measured. Meaning maximum leaching was supposed to had occurred till 1 cm depth as these samples had the dimension of 8 cm × 4 cm × 2 cm. With a maximum solution exposure of 144 days in the present investigation, maximum changes in the brick matrix were supposed to have occurred till a depth of ½ cm from the surface.
The small cubes from the brick halves (b) was subsequently dried at 105˚C until constant weight was obtained (24 hours) and crushed. 5.00 g of this crushed material was mixed with 12.50 mL distilled water and agitated for 24 hours on a shaking table.

5 RESULTS AND DISCUSSION

5.1 Measurement of pH and electrical conductivity in the brick matrix

The effect of the exposure to solutions with pH 3-11 on the pH and electrical conductivity in the brick matrix was examined and outlined in figure 1a and 1b.

The results for the pH in the matrix in figure 1a showed a tendency for the bright colors being in top of the graph representing exposure to solutions with high pH just as a tendency for darker colors representing exposure to solutions with low pH and pH 7 being in the bottom of the graph. It is to be noticed that all measured values are higher or equal to the pH in the reference brick not being exposed to any solution at all. According to the theory, emission of the alkali ions from the brick matrix results in increased pH which can neutralize the exposure from the acidic solution. Additional it is

seen that for bricks submerged in solutions with high pH there was no possibility for neutralization and in this case pH increases in the matrix.

Regarding the measured electrical conductivity in figure 1b there is a tendency for the bright colors being in the top of the graph representing brick specimens being submerged into solutions with high pH values just as there is a tendency for the darker colors being in the bottom of the graph. The results of bricks submerged in solution with pH 7 have most similarities with the bricks specimens submerged into solutions with low pH (pH 3 and pH 5). This indicates that the water soluble ion content is almost unchanged in the brick specimens who had been submerged to solutions with pH 11 in contrast to the brick specimens which was submerged into solutions with pH 3, 5 and 7 where a reduced electrical conductivity was measured. The results for the brick specimens with pH 9 do not follow any of these patterns; the samples were measured twice though with the same result.

Regarding the measured electrical conductivity, only the water soluble fraction was measured. It would have been informative to take out water samples from the solutions to measure changes in this solution as a function of submersion duration and to make a disaggregation of the brick matrix to measure the non-water soluble ion contents remaining in the brick matrix.

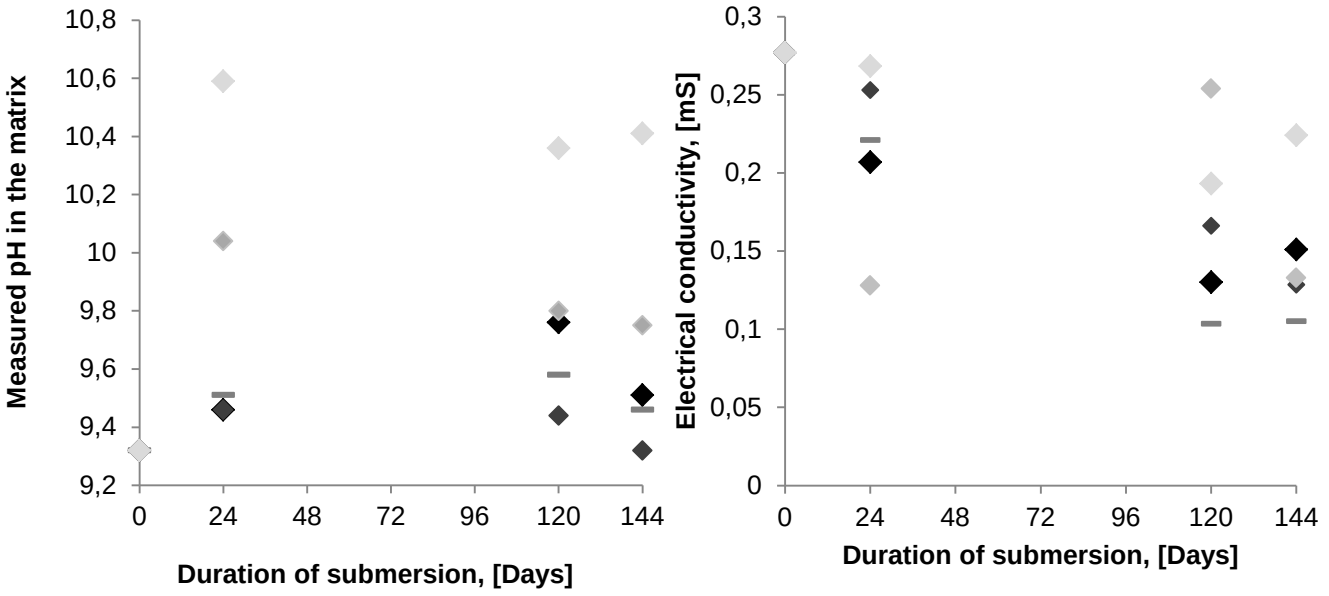


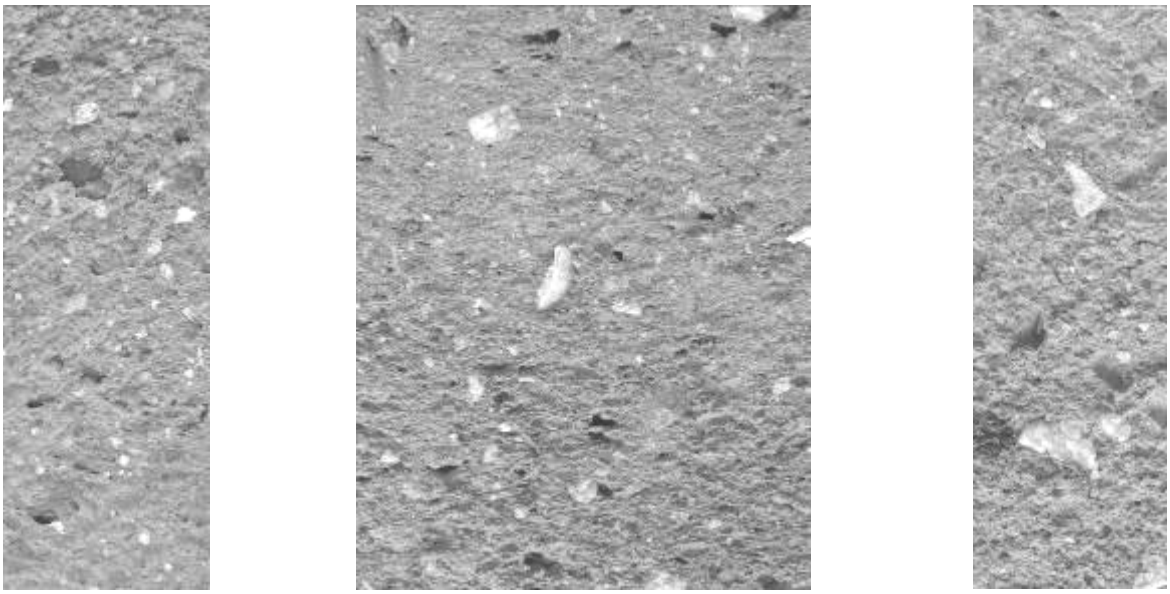
Figure 1. Measured a) pH and b) Electrical conductivity in the matrix as a function of the duration the bricks were submerged into the solution with pH 3 (◆), pH 5 (◆), pH 7 (—), pH 9 (◆) and pH 11 (◆).

On basis of the results for the water soluble ion content and pH in the matrix it is indicated that solely measuring the pH only would give limited of the weathering degree as relative small pH changes occurs simultaneously with significant matrix changes here represented by water soluble ion content.

This means that as a minimum also the electrical conductivity should be measured too however whether this is satisfying describing or measurement of each of the ion contents is necessary too is unknown but is investigated at present.

5.2 Macro pictures of the exposed surfaces

The possible weathering of the brick matrix when exposed to solutions with different pH was also investigated by making macroscopic pictures of the exposed surfaces. See figure 2.



(a) **(b)** **(c)**

Figure 2. Macroscopic pictures of the exposed surfaces submerged a solution with into pH 3 (a) and pH 11 (c) for 144 days compared with a reference brick (b).

The pictures in figure 2 are shown in grayscale as it represent the surface most accurate. The reference specimen in figure 2b shows a relative smooth surface with minor holes and relative big grains. The brick specimen submerged into a solution with pH 3 for 144 days still possessed a relative smooth surface though also seemed to have relative more and relative bigger holes and an absence of the biggest grains. Figure 2c showing a brick specimen submerged in a solution with pH 11 for 144 days did not seem to have an increased amount of holes nor smaller or bigger. This brick specimen also included the relative big grains as in the reference specimen, however the surface did not seem just as smooth as the reference brick, in contrast it seemed as it is more uneven.

According to the theory ion exchange should had happened in acidic environment here represented by the apparently increased number and size of holes in figure 2a whereas break down of the interconnected glassy phase should occur in alkaline environment resulting in flaking in layers of the exposed surface which seems to be the case in figure 2c. These macroscopic pictures seems to visualize the theory. However, these macroscopic pictures can only give an overview and indications of the specimens. At present polished sections are prepared making possible a more accurate investigation of the eventual changes in the brick matrix as a consequence of the submersion in solutions with different pH.

5.3 The macroscopic effect

In figure 3 the results from the capillary suction are shown.

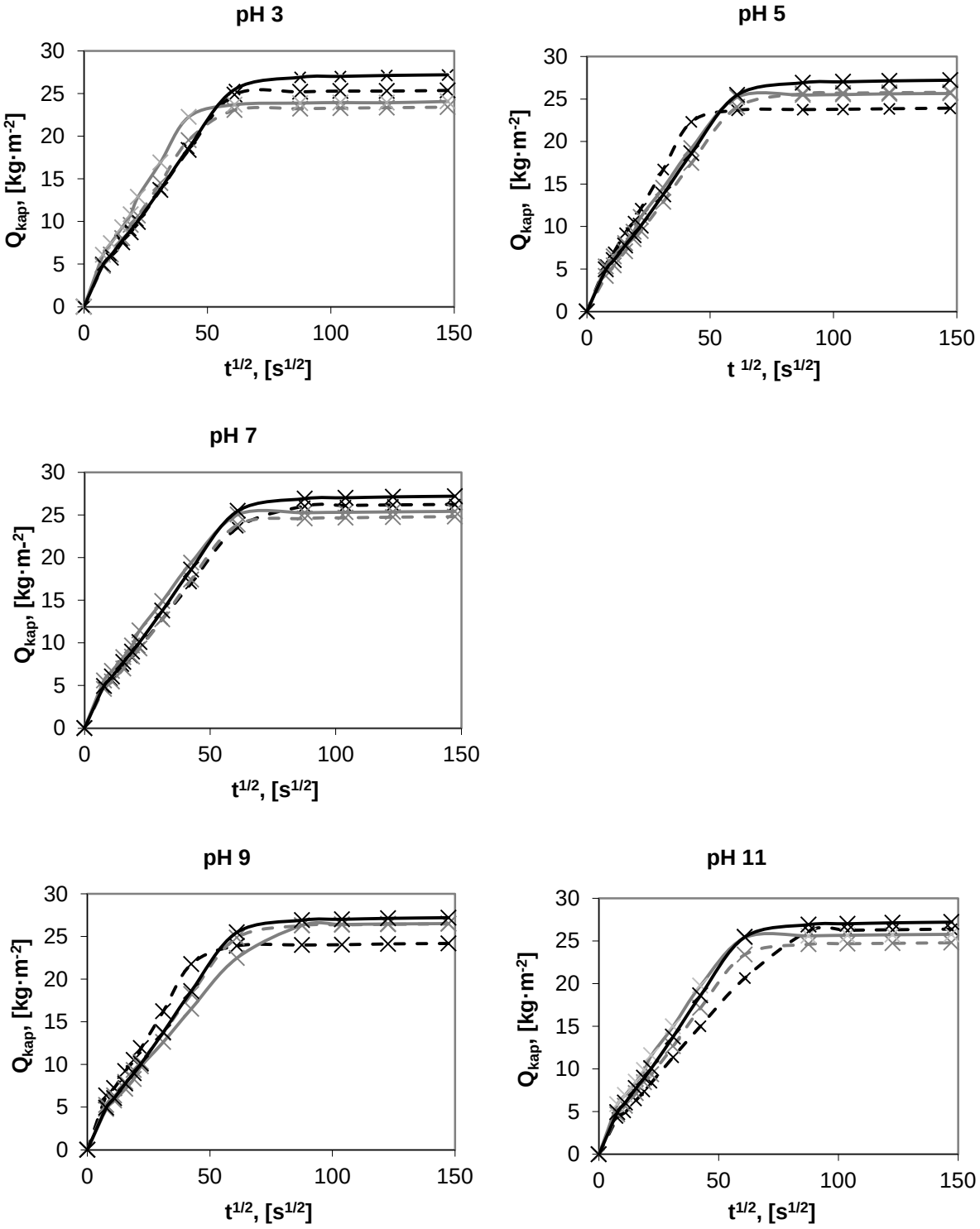


Figure 3. Capillary suction. In each graph is a reference brick (black) and three bricks with different submersion duration (24 days is shown as black dotted, 120 days as grey dotted and 144 days as grey) into a solution with a) pH 3, b) pH 5, c) pH 7, d) pH 9 and e) pH 11.

Table 2. Saturation coefficient, open porosity, density and water saturation coefficient

	Saturation coefficient	**Porosity**	**Density**	**Water saturation coefficient**
Reference	14.0 +/- 0.1	34.1 +/- 0.7	1750	0.46 +/- 0.02
Submerged into a solution with pH 3	13.6 (12.6) 12.7	34.0 (33.2) 33.1	1710 (1706) 1745	0.45 (0.48) 0.55
Submerged into a solution with pH 5	12.5 (13.3) 13.5	32.5 (33.2) 34.1	1760 (1772) 1750	0.56 (0.42) 0.47
Submerged into a solution with pH 7	13.9 (13.0) 13.6	34.4 (34.1) 34.4	1735 (1728) 1715	0.42 (0.42) 0.43
Submerged into a solution with pH 9	12.7 (13.9) 13.9	33.3 (33.6) 34.5	1753 (1749) 1738	0.54 (0.44) 0.39
Submerged into a solution with pH 11	13.7 (13.4) 13.7	33.8 (34.2) 34.4	1766 (1693) 1721	0.36 (0.42) 0.49

Capillary suction describes the macroscopic material as a whole and its interconnections. Small pores take up water slowly, however has relatively higher maximum water content than materials with smaller pores. However, local changes in the material as relatively higher changes in the material areas close to the surface in relation to material from inner areas is not clearly identified.

In each of the graphs a-e in figure 3, a reference line is added which is an average of 4 experiments with capillary suction from [8] not submerged in any solution prior to the capillary suction. In figure 3a showing the results of the capillary suction for the brick specimens submerged into a solution with pH 3 for 24, 120 and 144 days a higher initial water uptake and a lower final water uptake is seen compared to the reference brick specimen. This indicates that the pore size has been enlarged as a consequence of the submersion of the brick specimens into the solution. The same tendency is seen in figure 3b representing brick submersion into a solution with pH 5, however less pronounced. The brick specimens that was submerged into a solution with pH 7 (figure 3c) all had the same pattern and slope only showing minor parallel differences representing differences in the original brick structure. Brick specimens submerged into solutions with pH 11 possessed a higher initial water uptake followed by a reduced maximum water uptake compared to the reference bricks. This indicated an increased pore size as a consequence of the exposure to solutions with pH 11. The result of the submersion of the brick specimens into a solution with pH 9 showed in figure 3d are insignificant.

In table 2 are the calculated saturation coefficient, open porosity, density and water saturation coefficients shown. The saturation coefficient represents the final total water uptake related to the dry mass. As the reference value is 14.0 wt% and since only lower contents have been measured (especially at pH 3) this suggests varying increase in the pore size. Due to the high deviation in the reference porosity and due to the present values mainly are within these deviations with an absence of systematic changes from the reference values it is difficult to make any conclusions regarding this parameter. Densities as low as 1750 kg $\cdot$ m^{-3} have previously been measured for bright bricks. Regarding the brick specimen submerged into the solution with pH 11 it seems like a significant decrease in the density had happened suggesting an increase in porosity or peeling of parts of the original matrix, however this tendency is insignificant in table 3. The water saturation coefficient is a measure for the approximated linear water uptake velocity until the maximum water uptake has been reached and shows a significant increased water saturation coefficient at pH 3 and pH 11 after 144 days of exposure time also likelifying an increase in the pore size.

In general it is noticed that the results from the bricks only submerged into the solutions for 24 days (black dotted line) in some cases shows other tendencies than the bricks submerged 120 and 144 days into the different solutions. This is attributed to the fact that this shorter exposure time had minor influence on the bricks and that these variations is caused by original material variation.

The combination of the in-homogen brick material and the apparently limited overall macroscopic effect makes it difficult to make clear conclusions. Though it is obviously that changes had occurred since the deviation in the present results are much higher than in the reference experiments. The material variations influence on the results is in consistence with [5] which point out that the weathering rates vary dramatically with the mineral structure and composition. Those silicate materials which dissolve slowly tend to contain an extensively cross-linked structure. Silicates with a poorly connected fabric tend to dissolve rapidly and uniformly. The dissolution rate varies considerably with solution pH, as well as with mineral and solution compositions. Furthermore, most natural minerals are so impure that it is impossible to generate a truly homologous series of structure for study. For these and other reasons, rates measured by different experiments are commonly not comparable.

The present experiments were carried out at room temperature, though varying temperatures also has a significant effect on the deterioration. According to [4] a temperature increase of 20 K will result in the attack will increase with a factor 10.

The present study was carried out by submersion of the brick samples into solutions with different pH representing rain water at different conditions. Though as pointed out by [3] do the different components in a masonry structure influence each other. This is also the case by existence of materials only differing in pH and occasionally subjected to wetting. Bricks traditionally having a pH of 9 to 10 [2], carbonated lime a pH of 7.7, decreasing from pH 12.4 in the early stage of carbonation to 9.4 in the final stage of carbonation [9]. Uncarbonated cement mortar (ordinary Portland cement; water; w/c = 0.42; a/b = 1.67) has a pH of 12.8-13.0 [10].

By brick laying water from the mortar will enter the brick. In addition the persistent contact between mortar and brick must have an effect on the brick to some degree as the submersions of the brick into a solution with pH 11 until carbonation. Besides the different pH the exposure time has also an effect as shown in the present work.

Taking the present investigation and the theory into account increasing deterioration occurs by exposure to pH with increasing difference to the original state, though being aware pH can be as high as 13 in cement it would be highly relevant also to examine the influence on bricks at such high pH.

6 CONCLUSION

Even though chemical exposure is one of the main reasons for deterioration of bricks it has been limited investigated so far. In the present work the effect of extreme exposure was investigated by submerging the brick specimens into solutions with pH 3, 5, 7, 9 and 11 for 24, 120 and 144 days respectively.

The results for saturation coefficient, open porosity, density, water saturation coefficient, pH, electrical conductivity and macroscopic pictures of the exposed surfaces did each make indications of changes in the original brick matrix, though in unison and compared with the literature it seems reasonable to conclude that ion exchange in the brick matrix occur at low pH whereas at high pH the surface is peeling.

The ion exchange was most pronounced conspicuous in the results for the water soluble ion content represented by the electrical conductivity which in neutral and acid environment had been reduced to half the original amount but also visual convincing was the macro picture. The surface peeling at high pH was especially measured to have an influence on the density but was also visible on the macro pictures.

These changes were shown to be substantial on the original brick matrix and should be taken into account.

7 FUTURE WORK

In the present work some tendencies were shown, however to investigate the full possible influence of the exposure to solutions with different pH it would be beneficial to increase the exposure time of the bricks in the solutions and therefore additional bricks are to be submerged to solutions with pH 3, 5, 7, 9, 11 until an exposure time of 288 and 432 days have been reached.
In addition, as cement can have a pH as high as 13 and to clarify possible effects of contact between bricks and cement an experimental series with bricks submerged in a solution with pH 13 are to be initiated. Also examination of polished sections with SEM/EDX and measurements of each of the ionic contents in the brick matrix are to be carried out.

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REFERENCES

[1] Schumann, I.: *Zur nachträglichen Bestimmung der Brenntemperatur und zum Einfluss der Brenntemperatur auf die chemische Beständigkeit von Ziegeln.* PhD-Thesis, Technischen Universität Hamburg-Harburg, 1997. Shaker Verlag: Hannover 1997.

[2] Rörig-Dalgaard, I.: *Preservation of murals with electrokinetic – with focus on desalination of single bricks*. PhD-Thesis, Technical University of Denmark, 2009. Lyngby 2010.

[3] Charola, A.E. & Lazzarini, L: Deterioration of Brick Masonry caused by acid rain, Chapter 17. In: *Materials Degradation Caused by Acid Rain*, ed. ACS Symposium Series, Vol. 318, American Chemical Society: 1986, 250-258.

[4] Scholze, H.: *Glas – Natur, Struktur und Eigenschaften*. Springer-Verlag: Berlin Heidelberg New York 1977.

[5] Casey, W.H. & Bunker, B.: Leaching of Mineral and Glass Surfaces During Dissolution. *Mineral-Water Interface Geochemistry*, 23 (1990), 397-426.

[6] Duffer, P.: Effects of Glass Reactivity, Surface Corrosion. *American Ceramic Society Bulletin*, 73 (1994), 80-83.

[7] Karius, V. & Hamer, K.: pH and grain-size variation in leaching tests with bricks made of harbour sediments compared to commercial bricks. *The Science of the Total Environment,* 278 (2001), 73-85.

[8] Rörig-Dalgaard, I.: Further developments of a poultice for electrochemical desalination of porous building materials: Minimization of side effects. *Materials and Structures* (submitted) (2014).

[9] Cizer, Ö.; Rodriguez-Navarro, C.; Ruiz-Agudo, E.; Elsen, J.; Gemert D.V & Van Balen, K.: Phase and morphology evolution of calcium carbonate precipitated by carbonation of hydrated lime. *Materials Science,* 47 (2012), 6151-6165.

[10] McPolin, D.O.; Basheer, P.A.M. & Long, A.E.: Carbonation and pH in Mortars Manufactured with Supplementary Cementitious Materials. *Materials in Civil Engineering,* 21 (2009), 217-225.